NON-GASSING NICKEL-CADMIUM BATTERY ELECTRODES AND CELLS

Report No.: 712-122-3

Third Quarterly Report
15 December 1971 to 15 March 1972

Prepared by E. Luksha and D.J. Gordy Approved by C.J. Menard

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Jet Propulsion Laboratory
Contract No. 953184

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ABSTRACT

Supposedly long-lived nickel-cadmium batteries often fail due to severe gassing on charge. In order to increase the lives of such cells attempts are being made to construct "nongassing" positive and negative electrodes. In the third quarter of the program the gassing characteristics of both electrodes in negative limited cells was determined as a function of charge rate, charge temperature, and loading. Cycle life tests, up to 70 cycles, of some of the cells show they operate in a nongassing manner with very low degradation rates.

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I. SUMMARY

There are various special applications for very long-lived, a decade or more, sealed nickel-cadmium batteries. The gassing which normally occurs in such cells limits their lives sever. and in many cases is the sole cause of failure. An approach toward dramatically increasing their lives is to incorporate electrodes in these batteries that exhibit little or no gassing with controlled charge input.

This requires: 1) the ratio of positive to negative active material ratio be changed to make cells negative limited, and 2) use materials that possess the highest possible over-potentials for the hydrogen evolution reaction so that the onset of hydrogen gassing would result in a large voltage step to be used to cut off the charge.

This report describes work conducted during the third quarter towards this end. Small negative limited cells with different configurations of cadmium electrodes were tested. The gassing characteristics of the nickel and cadmium electrodes were determined as a function of charge rate, charge temperature, and cadmium electrode loading.

The key highlights of the work conducted in the third quarter was the cycling (70 cycles at 100% depth of discharge) of small negative limited cells constructed with electrodeposited cadmium active masses on silver and cadmium screens. The cells are operating in a nongassing manner judging from cumulative volume determination after an initial conditioning period. The degradation rate of these cells, presumably due to cadmium electrode fading, is 0.2% cycle and decreasing with cycling. The test data generated was used to select two designs of non-gassing cells of approximately 30 Ah capacity negative limited cells.

II. INTRODUCTION

There is presently a need for very reliable and very long lived, about one decade, secondary batteries for applications such as in deep probe space vehicles, medical implantations, various cordless appliances, and other special uses. Sealed nickel-cadmium batteries are uniquely suited for such applications, mainly because of their long lives. However, the gassing that normally occurs in these cells, limits their reliability for very long life. The gassing problem becomes particularly severe during latter stages of the cell life. Aging effects on both electrodes can result in a set of circumstances that sealed cells can rupture due to hydrogen generation on charge. In many cases, gas evolution is the sole cause of life limitation of nickel-cadmium cells. As a result, an approach toward increasing the life of nickel-cadmium cells toward the decade or so required, is to construct cells designed with little or no gassing. The Jet Propulsion Laboratories have suggested an approach leading to the development of a "nongassing" nickel-cadmium battery. Their approach involves essentially three changes in the design of conventional nickel-cadmium batteries. These are:

1. Change the ratio of positive to negative active material in the cells so that the cells become negative limited.
2. Use a grid material for the cadmium electrode that has a high overpotential for the hydrogen evolution reaction so that the onset of hydrogen gassing would be signaled by a relatively large voltage step.
3. Incorporation of a miniature electronic charge control device that will be used externally to each cell to end the charge using the voltage step as a signal.

Gould Inc., Energy Technology Laboratories, under subcontract to JPL is involved in the design, development, and testing of a "nongassing" battery in accordance with parts 1 and 2 above.

To reach these goals, cadmium electrodes with the highest possible overpotential for the hydrogen evolution reaction are being developed. Five configurations were suggested by Gould as holding forth the most promise. These are:

1. An electrodeposited cadmium active mass on an expanded cadmium metal screen.
2. A cadmium active mass deposited in a porous silver substrate of precisely controlled porosity and pore-size.
3. An electrodeposited cadmium active mass on an expanded silver screen.

4. A pressed cadmium electrode prepared from electrolytic $Ch(OH)_2$ admixed with gold or silver powder.

5. Other novel materials with high overpotential for H_2 evolution reaction.

These various configurations are to be tested to determine the optimum configuration for minimum gassing as a function of temperature, charge and discharge rates, and loading. In addition, the program includes the determination of the gassing characteristics and specific capacities of state-of-the-art nickel electrode in order that the best nickel electrode from gassing and energy density considerations be employed for the proposed nongassing cell. A 3^3 full factorial experimental design is being employed for the collection of the above-mentioned data.

III. RESULTS AND DISCUSSION

In previous work describing the development of a nongassing nickel-cadmium battery, the preparation[1] of several varieties of cadmium electrodes; namely, electrodeposited cadmium active mass on silver and cadmium screens and a cadmium active mass on a sintered silver substrate was outlined. Also, the testing of positive electrodes to determine their gassing characteristics as a function of charge rate, charge temperature, and $Ni(OH)_2$ loading was done. The work conducted in the third quarter, and described herein, was concerned with the testing of the above mentioned cadmium electrodes in small negative limited cells using a previously described test installation[2]. The testing involved the determination of the H_2 and O_2 evolution rates in such cells as a function of charge rate, discharge rate, discharge temperature, and cadmium electrode loading.

A. Performance of Electrodeposited Cadmium Electrodes On Cadmium Screen

The gassing characteristics were determines of both the cadmium and nickel electrodes in negative limited cells constructed with electrodeposited cadmium active mass on a cadmium screen in accordance with the experimental design shown in Table 1. These cells were constructed with two nickel electrodes of 20 g/in.[3] loading. The experiments at the median temperatures, 25°C, circled in Table 1 were not performed. Representative gassing data obtained at the 151 mA charge rate at 0° and 50°C charge temperature are shown in Figures 1 and 2. These are semi-log plots except at the break at zero current to allow representation of no gassing. In both figures hydrogen appears abruptly when the electrode reaches full charge. The evolution of hydrogen is accompanied by a potential step. In Figure 1 it is noted that no oxygen was detected, while in Figure 2 oxygen was evolved before end-of-charge. This is due to the very high efficiencies of the cell cadmium electrodes at the high temperature. The states-of-charge, Q, at which hydrogen and oxygen were first detected at the third and twentieth cycle are shown in Table 2. The cycle data was obtained at the high temperature only. Aside from the considerable scatter in the experimental data, several noteworthy features are evident. There is an increase in the gas-free capacity of the cadmium electrode with increasing charge temperature. The cadmium electrodes tested in this portion of the program had abnormally high efficiencies at the high temperature, some as high as 150%. It was previously shown that the oxygen gassing occurred at lower states-of-charge on nickel electrodes charged at higher temperatures. The combination of higher gas-free capacity on the cadmium electrode and lower gas-free capacity on the positive electrode, makes the high temperature gas-free operating condition more tortuous than previously expected.

Also, there are indications of negative electrode "fading" by the change in the gas-free capacity of the cadmium from the third to the twentieth cycle. There is a considerable uncertainty in the magnitude of "fading" to be expected. The best estimates at the operating conditions described above are given in Table 3.

TABLE 1. EXPERIMENTAL DESIGN FOR STUDY OF GASSING IN NEGATIVE LIMITED CELLS

Experimental Parameters and Limits for Cell Gassing Study

		LEVELS		
		+	0	–
X_1	Charge Temperature, °C	50°	25°	0°
X_2	Charge Current Density, A/in.^{2}	0.29	0.17	0.06
X_3	Nickel Electrode Loading, Ah/in.^{2}	0.30	0.20	0.10

3^3 Full Factorial Experiment for Study of Nickel Electrode Gassing

EXP NO.	X_1	X_2	X_3	EXP NO.	X_1	X_2	X_3
1	+	+	+	15	–	0	0
2	0	+	+	16	+	–	0
3	–	+	+	17	0	–	0
4	+	0	+	18	–	–	0
5	0	0	+	19	+	+	–
6	–	0	+	20	0	+	–
7	+	–	+	21	–	+	–
8	0	–	+	22	+	0	–
9	–	–	+	23	0	0	–
10	+	+	0	24	–	0	–
11	0	+	0	25	+	–	–
12	–	+	0	26	0	–	–
13	+	0	0	27	–	–	–
14	0	0	0				

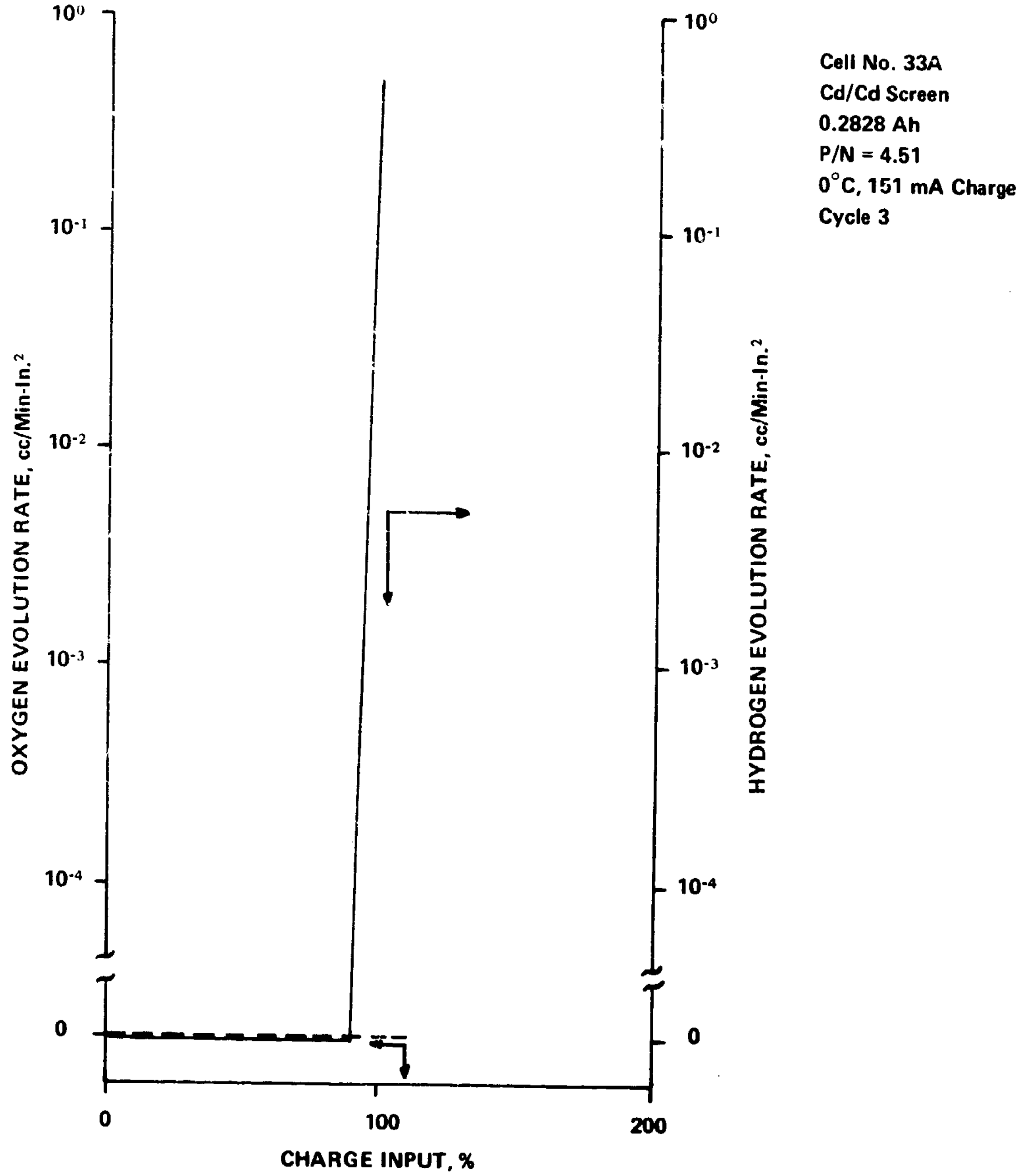

FIGURE 1. HYDROGEN & OXYGEN EVOLUTION RATES IN NEGATIVE LIMITED CELLS WITH ELECTRODEPOSITED CADMIUM ON CADMIUM SCREEN

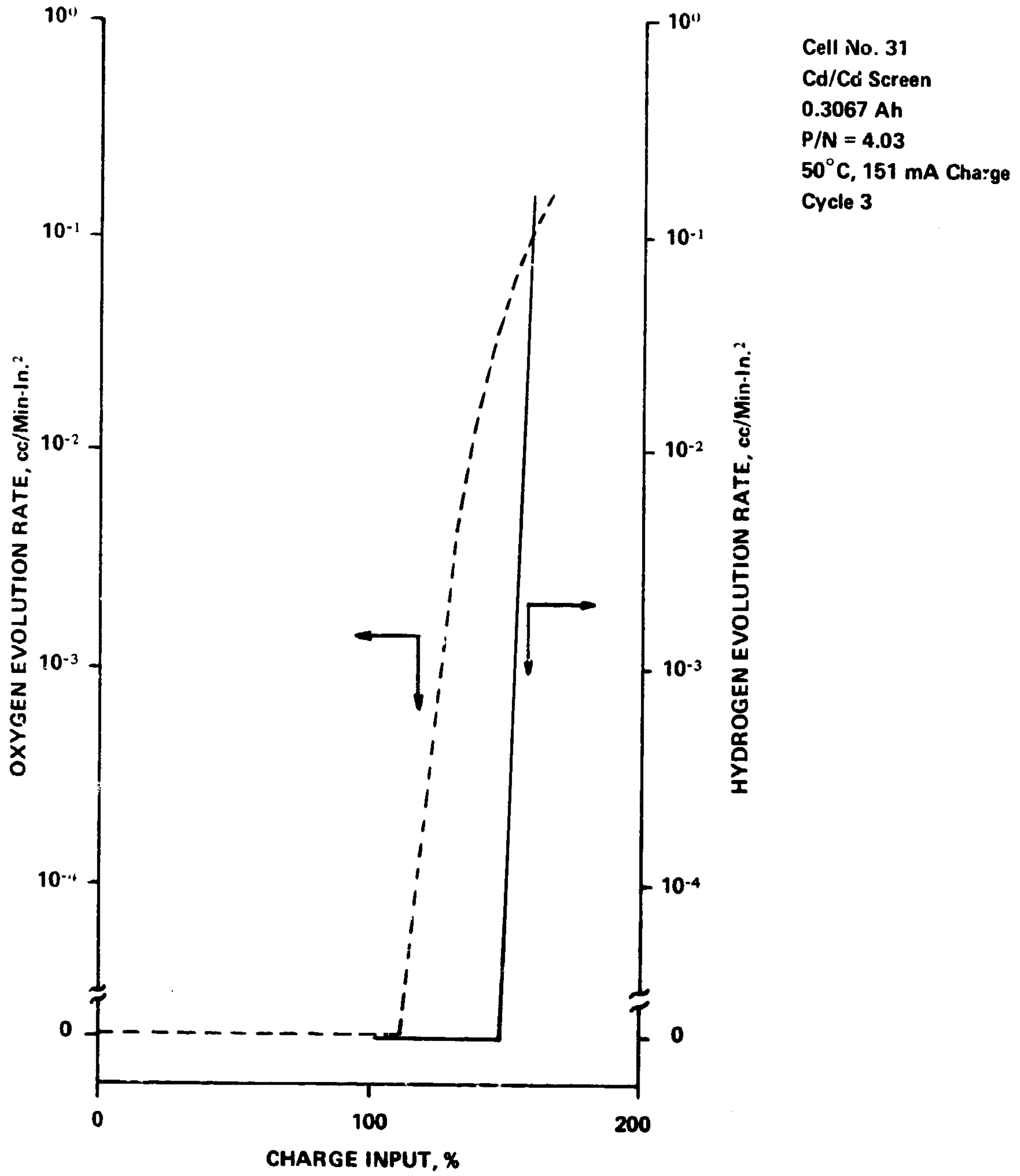

FIGURE 2. HYDROGEN & OXYGEN EVOLUTION RATES IN NEGATIVE LIMITED CELLS WITH ELECTRODEPOSITED CADMIUM ON CADMIUM SCREEN

TABLE 2. SUMMARY OF RESULTS

State-Of-Charge, Q, When Gassing Was First Detected In Negative Limited Cells
Cd On Cd Screen
Q_3 = 3rd Cycle
Q_{20} = 20th Cycle

Exp No.	X_1	X_2	X_3	H_2 Evolution %Q_3	H_2 Evolution %Q_{20}	O_2 Evolution %Q_3	O_2 Evolution %Q_{20}
1	+	+	+	126	93	12	30
3	–	+	+	25		30	
4	+	0	+	100	110	32	28
6	–	0	+	75		40	
7	+	–	+	140	94	22	16
9	–	–	+	94		50	
10	+	+	0	150	104	17	29
12	–	+	0	42		15	
13	+	0	0	112	110	22	16
15	–	0	0	88		21	
16	+	–	0	116	118	23	24
18	–	–	0	95		43	
19	+	+	–	150	100	12	17
21	–	+	–	93		20	
22	+	0	–	125	100	26	19
24	–	0	–	96		22	
25	+	–	–	148	41	27	(?)
27	–	–	–	94		23+(?)	

? Oxygen Not Generated

TABLE 3. EFFECTS OF CHARGE CURRENT AND LOADING ON CADMIUM ELECTRODE "FADING"

Variables (Linear)	Efficiency Loss (20 Cycles)
Charge Current	7
Loading	17
Charge Current-Loading	–10
Variables (Quadratic)	
Charge Current	–39
Loading	–22
Charge Current-Loading	–50

Very large quadratic effects are apparent indicating that the median levels of charge and loading are preferred to minimize fading for this particular configuration of negative electrodes.

Also of interest in Table 2 are the states-of-charge at which oxygen is first detected in the negative limited cells. Since cells were constructed with at least a P/N ratio of 2:1, the detection of oxygen at the rather low states was somewhat of a surprise. No thorough comparison between this set and previous data on nickel electrode gassing has been made yet. However, it was observed that these cells operated at higher voltages on charge. This was due to the use of cadmium screen and tabs. As a result, we believe that gassing even on the positive electrodes may be promoted by the increased internal cell resistance perhaps due to the use of cadmium contacts which increase the internal resistance over the conventional nickel tabs and plaques. As a result, in the future every effort will be made to minimize internal cell resistance via the use of over-designed contacts and current collectors. Otherwise, gassing rate could be influenced by relatively high internal cell resistance.

The effects and interactions of the variables are given in Table 4. It is seen that the most important variable as far as hydrogen evolution is the charge temperature, with gassing at higher states-of-charge at the higher temperatures. The other variables, charge rate, loading, and interactions have far less important effects.

TABLE 4. EFFECTS OF VARIABLES AND INTERACTIONS ON GASSING IN NEGATIVE LIMITED CELLS – Cd On Cd SCREEN

Variables (Linear)	H_2 Evolution, $\%Q_3$
Charge Temperature	39
Charge Current	−8
Loading $Cd(OH)_2$	−12
Charge Temp – Current	16
Charge Temp – Loading	3
Charge Current – Loading	−9
Variables (Quadratic)	
Charge Current	7
Loading $Cd(OH)_2$	5

B. Performance of Electrodeposited Cadmium Electrodes on Silver Screen

A set of data similar to the one described above for the electrodeposited cadmium active mass on a cadmium screen was obtained for electrodes prepared in a manner that was identical except that they contained a silver screen rather than a cadmium screen. Representative gassing data obtained for these particular cells at 151 mA charge at 0° to 50°C are shown in Figures 3 and 4. Once again these are semi-log plots except at the break at the origin to allow for representation of no gassing. A summary of all the test data, primarily the state-of-charge at which

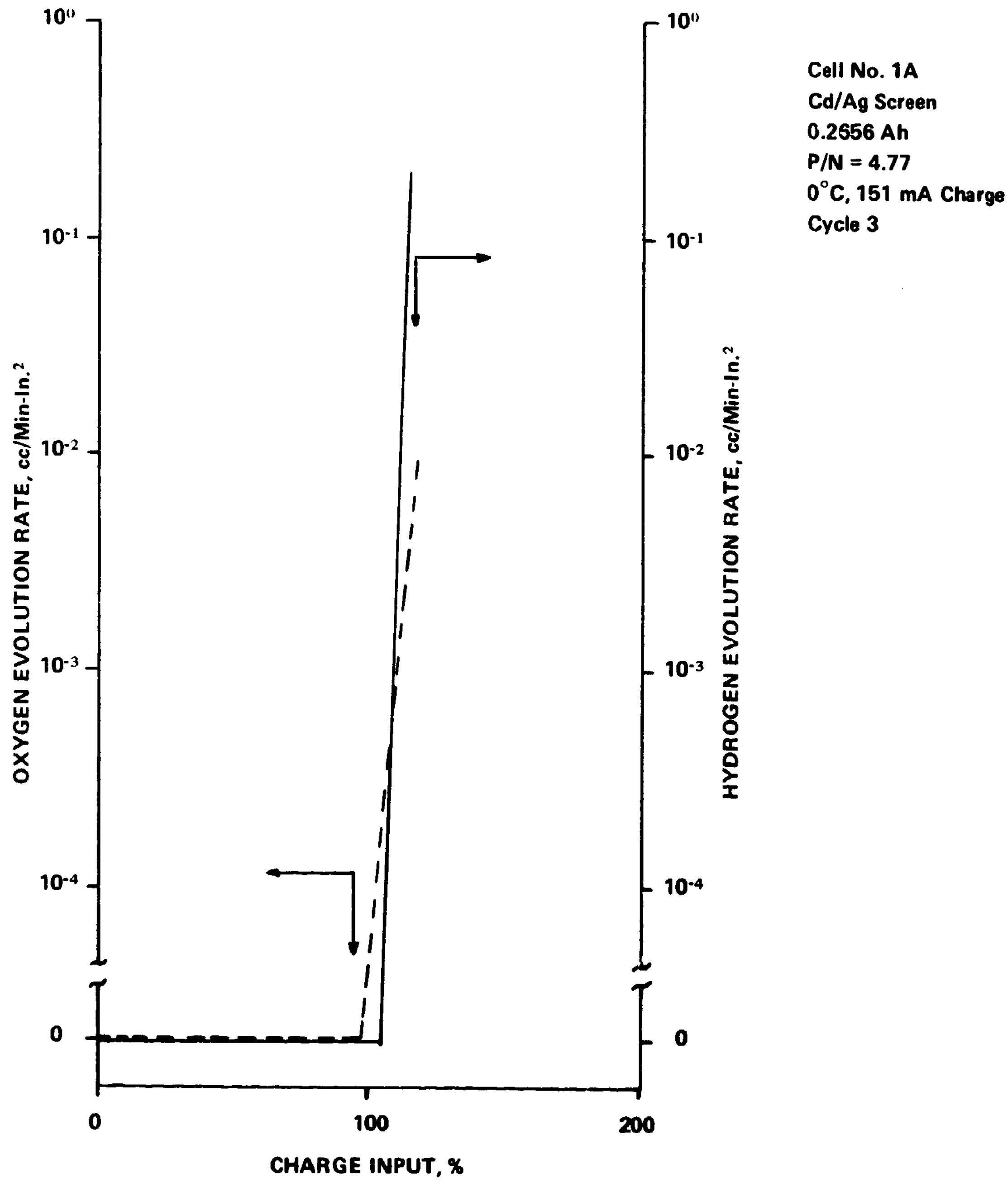

FIGURE 3. HYDROGEN & OXYGEN EVOLUTION RATES IN NEGATIVE LIMITED CELLS WITH ELECTRODEPOSITED CADMIUM ON SILVER SCREEN

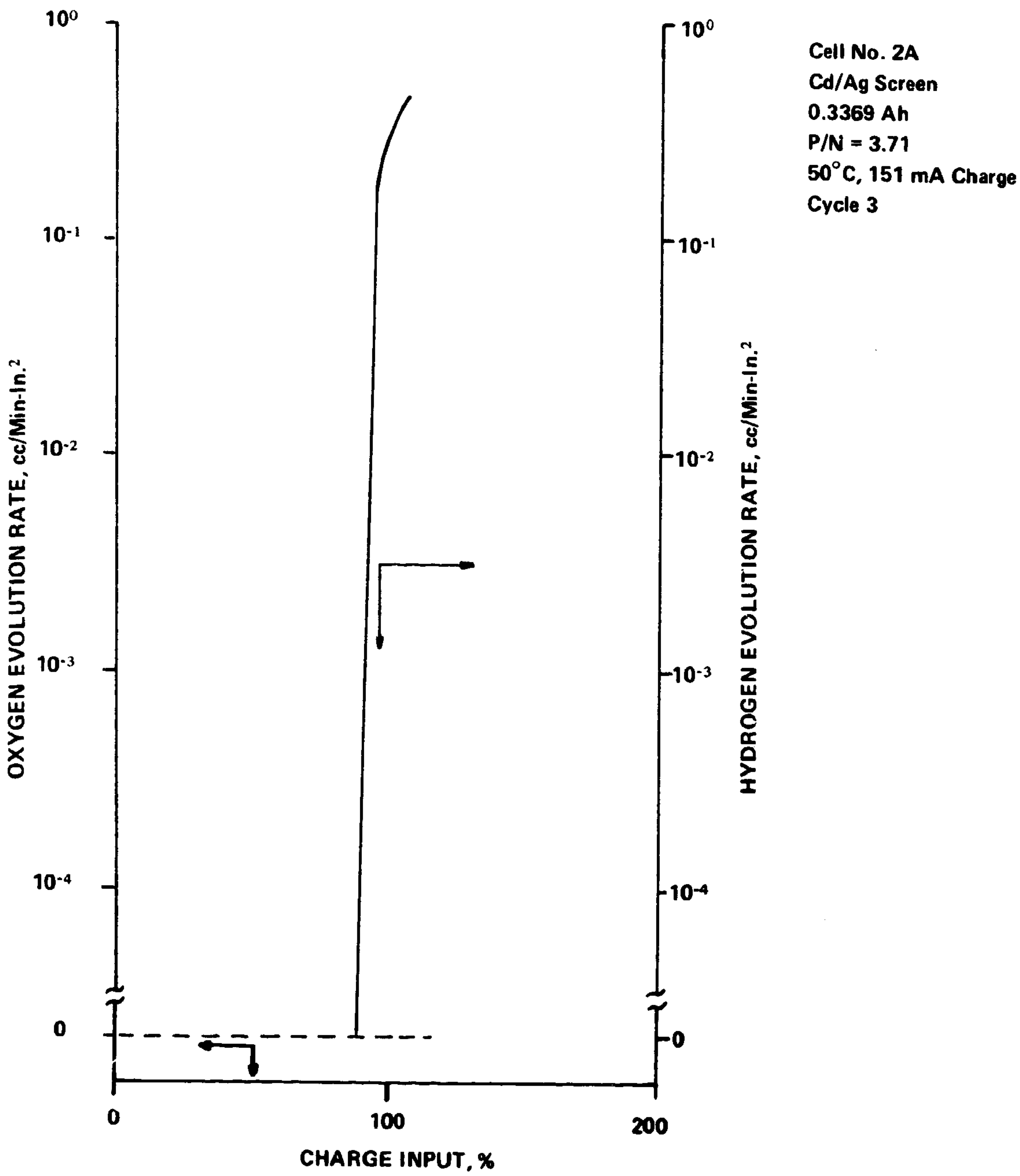

FIGURE 4. HYDROGEN & OXYGEN EVOLUTION RATES IN NEGATIVE LIMITED CELLS WITH ELECTRODEPOSITED CADMIUM ON SILVER SCREEN

gassing was first detected on the positive and negative electrodes is given in Table 5. It is immediately apparent that the cadmium prepared electrode with the silver screens have lower gas-free capacities than their cadmium screen counterparts. The overall average for the cadmium screen electrodes was $\%Q_3$ = 104 and the overall average for silver screen set was 85%. Also of importance was the state-of-charge at which oxygen was evolved on the nickel electrodes on an overall average, gassed at 25% state-of-charge for cells prepared with cadmium screened electrodes and at 33% state-of-charge in cells prepared with cadmium electrodes containing silver screens. The difference is perhaps due to the lower cell operating potentials due to the improved current collection as a result of the use of the silver screen.

The effects of the variables and their interaction on hydrogen gassing in the cells is given in Table 6. Once again the charge temperature is seen to be an important factor governing cell efficiency, however to a lesser extent than observed for the cells containing the cadmium screens. As far as the other variables are concerned in view of the experimental uncertainty evident by comparing the results in Tables 4 and 6, it is not possible to unambiguously sort out the effects of the other variables.

At any rate, the use of an electrodeposited cadmium active mass on a silver screen is a promising electrode for use in the proposed nongassing cell.

C. Performance of Cadmium Electrodes Containing Sintered Silver Substrates

The preparation of cadmium electrodes from sintered silver substrates has been described in an earlier report. Some initial data in negative limited cells using such electrodes was also presented earlier[3]. Silver sinter based electrodes possessed initial efficiencies far lower than expected, in the range of 30-40% of weight gain rather than the 70% range expected. Aside from this particular difficulty, they performed as the other varieties of cadmium electrodes in negative limited cells. In view of the rather unsatisfactory results for such structures in a parallel effort[3-4], it was decided not to devote more time on this particular type of electrodes, because of the development work that would be required. However, the authors still regard silver sintered structures as extremely promising and worthy of attention if future efforts are to be made in the area of nongassing cells.

D. Pressed Cadmium Electrodes

Pressed cadmium electrodes were prepared by first plating cadmium metal onto a nickel foil, scraping it off, washing and drying it, and finally grinding it in a motorized mortar and pestle for 30 minutes. The resulting powder was blended with 15% by weight Teflon powder in a Twin–Shell blender. The resulting powder was pressed onto a cadmium screen at 6 ton/in.^{2} The initial performance and properties of these electrodes offered no apparent advantages over the electrodeposited types described in III.A and III.B and were therefore not tested further.

TABLE 5. SUMMARY OF RESULTS

State-Of-Charge, Q, At Which Gassing Was First Detected In
Negative Limited Cells = Cd on Ag Screen
= Q_3 = 3rd Cycle
= Q_{20} = 20th Cycle

Exp No.	X_1	X_2	X_3	H_2 Evolution $\%O_3$	O_2 Evolution $\%Q_3$
1	+	+	+	81	22
3	–	+	+	65	39
4	+	0	+	96	55
6	–	0	+	75*	39*
7	+	–	+	65	38
9	–	–	+	70	40
10	+	+	0	83	23
12	–	+	0	61	27
13	+	0	0	85	43+
15	–	0	0	50	22
16	+	–	0	93	37
18	–	–	0	72	31
19	+	+	–	96	27
21	–	+	–	75	16
22	+	0	–	160	48
24	–	0	–	102	26+
25	+	–	–	90	37+
27	–	–	–	105	21
				85	33

*Data Lost – Estimated Values

TABLE 6. EFFECTS OF VARIABLES AND INTERACTIONS ON GAS EVOLUTION IN NEGATIVE LIMITED CELLS – Cd/Ag SCREEN

Variables (Linear)	H_2 Evolution, %Q_1
Charge Temperature	15
Charge Current	– 3
Loading $Cd(OH)_2$	–15
Charge Temp – Current	5
Charge Temp – Loading	– 3
Charge Current – Loading	– 2
Variables (Quadratic)	
Charge Current	–15
Loading $Cd(OH)_2$	16

E. Cycle Life Of Negative Limited Nongassing Nickel-Cadmium Cells

Some cycle test data has been accumulated on nongassing negative limited cells constructed with electrodeposited cadmium active mass on silver and cadmium screens. Figure 5 shows some representative cycle data at 100% depth of discharge. During early cycling, the input-output efficiency is less than 100% due to an improper P/N ratio. After some cycling due to aging one or both electrodes, the fading of the negative electrode being a very likely contributor, the proper P/N ratio is established for a nongassing cell. No gassing, based on cumulative volume changes in the cell, could be detected. The rate of degradation, due to fading of the negative electrode, is in the range of 0.2%/cycle, which is tolerable value for the nongassing cell in its present state of development. This value for the degradation rate is in good agreement with the values obtained in previous work[5] on more conventional structures. Indications are that the degradation rate will decrease with further cycling.

Cell No. 43B
Charge at 452 mA to 1.75V
Discharged at 150 mA to 0.0V
Negative Theo. Capacity = 0.6657
Positive to Negative Ratio = 1.852:1
Electrodeposited Cadmium on Cadmium Grid
Room Temperature

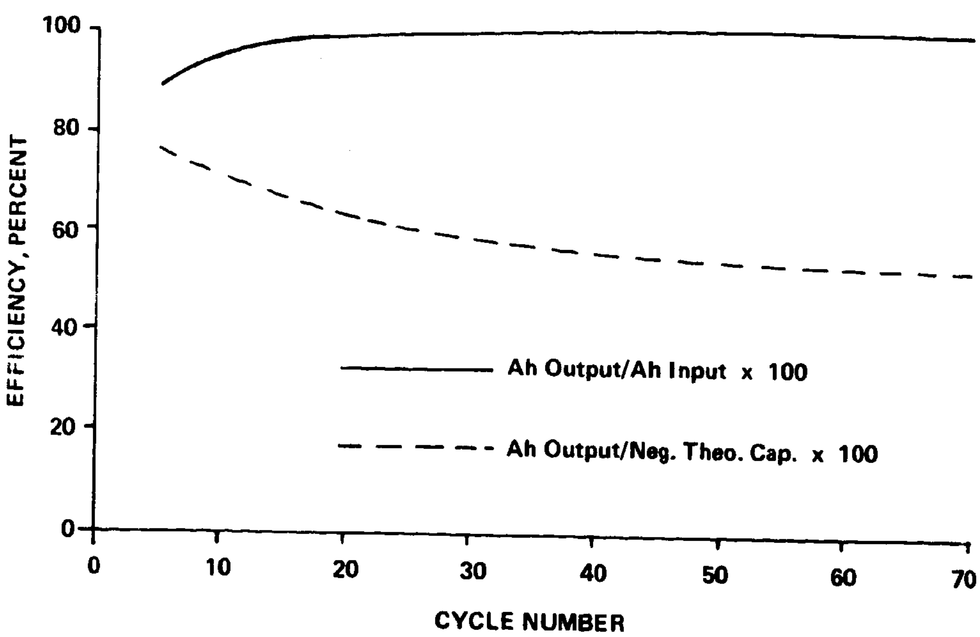

FIGURE 5. CYCLE LIFE OF NEGATIVE LIMITED NON-GASSING CADMIUM CELL – 100% DEPTH OF DISCHARGE

IV. CONCLUSIONS

The phase of the program to determine the gassing characteristics, for both positive and negative electrodes, in realistic negative limited cells, using various configurations of negative electrodes, has ended. The highlights of the third quarter are:

1. Nongassing negative limited cells have been made and some have received up to 70 cycles (100% depth of discharge) as of this report period. These cells are nongassing based upon cumulative volume measurement, after an initial conditioning period. The rate of degradation is small, about 0.2%/cycle and decreasing with cycling.

2. Electrodeposited cadmium active masses on silver and cadmium screens are the most promising electrodes tested in the program. They have excellent gassing characteristics in that they gas only at full charge. The gassing is also accompanied by a large potential step.

3. The lowest acceptable positive/negative active material ratios for present negative limited cells was observed to be 3:1.

4. The charge temperature was observed to be the most important variable governing cadmium electrode efficiency. High charge temperatures promoted higher gas-free outputs.

V. FUTURE WORK

Work scheduled for completion during the fourth quarter of the program is the construction and testing of batteries of approximately 30 Ah capacity. Tentatively, the designs summarized in Table 7 are the most likely prospects for nongassing batteries.

TABLE 7. ANTICIPATED OUTPUT OF CELLS

Negative	P/N Ratio	Capacity
Electrodeposited Cd/Cd Screen	5:1	26 Ah
Electrodeposited Cd/Ag Screen	3:1	33 Ah

The relatively high P/N ratios were chosen to assure no gassing under the worst test conditions. Actually, we have observed nongassing modes of operation with P/N ratios as low as 2:1. Both of the negative electrodes mentioned in Table 7 are to be the light-weight cadmium electrodes used in the study described in Section III. Although both the negative electrodes have the same loading, a higher ratio is required for the all-cadmium electrodes because of their higher output and the observed increased gassing rate of the nickel electrodes when used together with all-cadmium electrodes.

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